Bowman et al.

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[54]		ET DIFFUSION TRANSFER AGES AND PHOTOGRAPHIC 'S
[75]	Inventors:	Wayne A. Bowman; John F. Bishop; John M. Noonan, all of Rochester, N.Y.
[73]	Assignee:	Eastman Kodak Company, Rochester, N.Y.
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		430/536
[56]	-	References Cited
	U.S. P	ATENT DOCUMENTS
	4,071,366 1/1	975 Back et al

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4,097,282	6/1978	Noonan et al	430/215
4,113,493	9/1978	Sandru et al.	96/67
4,150,217	4/1979	Noonan et al	528/290
4,178,182	12/1979	Tsubota et al	96/73
4,190,447	2/1980	Coil et al	430/215

Primary Examiner—Edward C. Kimlin Attorney, Agent, or Firm—Harold E. Cole

[57] ABSTRACT

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Photographic elements, two-sheet diffusion transfer assemblages containing such elements, and dye image-receiving elements are described. The photographic element comprises a support, a neutralizing layer, a timing layer, a vinylidene chloride polymeric layer, a polymeric primer layer, and at least one silver halide emulsion layer having a dye image-providing material associated therewith. The vinylidene chloride polymeric layer and the polymeric primer layer prevent unwanted transfer of portions of the emulsion layer to a receiver when the receiver and photographic element are peeled apart. The polymeric primer layer can be either a particular ionic vinyl polymer or a particular ionic polyester.

21 Claims, No Drawings

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TWO-SHEET DIFFUSION TRANSFER ASSEMBLAGES AND PHOTOGRAPHIC ELEMENTS

This invention relates to photography, and more particularly to photographic elements and two-sheet photographic assemblages for diffusion transfer photography. In the photographic element, two primer layers are present between the silver halide emulsion layers 10 and the process control layers (timing layer and neutralizing layer). The primer layers comprise (1) a vinylidene chloride polymeric layer, and (2) a particular ionic vinyl polymer or ionic polyester layer which prevent unwanted transfer of portions of the emulsion layer to a 15 receiver when the receiver and photographic element are peeled apart.

In a two-sheet image transfer process, a photosensitive or donor element is employed along with a dye image-receiving element. The receiving element usually 20 comprises a support having thereon a dye image-receiving layer. The donor element comprises a support having thereon photosensitive silver halide emulsion layers having associated therewith dye image-providing materials. The donor element also contains process control 25 layers for terminating development after the required development has taken place. In general, the process control layers prevent any significant change in image formation from occurring beyond the optimum time required for development and useful transfer of dye. 30 Such layers include one or more timing and acid layers.

In practice, the donor element is exposed, soaked in an activator or processing composition, and then laminated to the receiving element. An imagewise distribution of dye image-providing material from the donor 35 diffuses to the receiving element. After a required period of time, the two elements are separated.

The physical parameters of this system are stringent. All layers of the donor and receiver must be uniformly coatable, be stable and have good wet and dry adhesion. 40 The donor element must retain physical integrity while soaking in a highly alkaline processing composition for ten seconds or more at elevated temperatures ranging up to 32° C. The donor element must uniformly unite with the surface of the receiving element and, after 45 passage through processing rollers, remain tightly in contact with the receiver without external pressure for the time required to transfer the dye image. This processing time may exceed ten minutes at temperatures which may vary over a wide range. Finally, the donor 50 and receiving element must be cleanly separable without appreciable effort and produce no surface distortion in the receiving element.

It has been difficult to simultaneously meet all of the above objectives in a two-sheet diffusion transfer assem- 55 blage. A problem of poor wet adhesion between the timing layer and the adjacent emulsion layer has been encountered which results in unwanted transfer of portions of the emulsion layer to the receiver when the donor and receiver are separated.

It would be desirable to provide a photographic element for a two-sheet diffusion transfer assemblage which does not have poor wet adhesion between the timing layer and the emulsion layers.

In U.S. Pat. Nos. 4,097,282 and 4,113,493, various 65 heat-activatable adhesive compositions are described for use in various photographic materials, including image transfer film units. These adhesive materials are

similar to various ionic polyesters which we have found to be useful as one of the polymeric primer layers in our invention.

In Research Disclosure 18452, August 1979, a vinylidene chloride polymeric layer is disclosed as a timing layer. In U.S. Pat. No. 4,061,496, the use of two timing layers is disclosed. One of these timing layers can be a vinylidene chloride polymer. The use of a vinylidene chloride polymeric layer in combination with an ionic polymeric layer as primer layers as disclosed herein is not described in these references, however.

We have found that the use of certain primer layer compositions provide good wet adhesion during the lamination period, does not increase the force required to separate the donor from the receiver after development, and does not transfer any of the emulsion layer to the receiver. These layers are coatable without special techniques, are stable and flexible, do not affect donor sensitometry, and do not materially affect the timing layer breakdown time.

In accordance with our invention, a photographic element is provided which comprises a support having thereon, in order, a neutralizing layer, a timing layer and at least one photosensitive silver halide emulsion layer having associated therewith a dye image-providing material, and wherein a layer of a vinylidene chloride polymer is present between said timing layer and said emulsion layer, and a polymeric primer is present between said vinylidene chloride polymeric layer and said silver halide emulsion layer, said primer layer comprising:

(A) an ionic vinyl polymer comprising 10 to 30 weight percent of recurring units which conform to the structure:

$$\begin{array}{cccc}
R \\
| & \\
CH_2-C+ & R^2 \\
| & & \\
COGR^1-N^{\oplus}-R^3 & X^{\ominus} \\
\downarrow & & \\
R^4
\end{array}$$

and 70 to 90 weight percent of recurring units which conform to the structure:

$$R$$
 $+CH_2-C+$
 $COGR^1OH$

wherein:

each R is independently hydrogen or methyl;

each R¹ is independently a straight or branched chain alkylene group of 2 to about 6 carbon atoms, such as ethylene, propylene, trimethylene or tetramethylene;

R², R³ and R⁴ are each alkyl or substituted alkyl group (including aralkyl, such as benzyl) of 1 to about 7 carbon atoms, such as methyl, ethyl, propyl, butyl or hexyl;

each G is independently oxygen or NH; and

X⊕ is an acid anion, such as chloride, bromide, acetate, methosulfate or p-toluenesulfonate; or

- (B) an ionic polyester comprising recurring units of:
- (I) a diol component which comprises:
- (a) at least 50 mole percent of units derived from diols having the structures:

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$$-O + OCH_2CH_2 \rightarrow_n O - OCH_2CH_2 \rightarrow_n OCH_2 \rightarrow_n OCH$$

wherein n is an integer of from 1 to 4; and

(ii) $O-R^6O-m$, wherein m is an integer of from 2 to 4, and R^6 is an alkylene group of 2 to about 4 carbon atoms, such as ethylene, propylene, trimethylene or tetramethylene; and

(b) 0 to 50 mole percent of units derived from one or more diols having the structure:

wherein R⁷ is an alkylene group of up to about 16 carbon atoms, such as ethylene, propylene, trimethylene, tetramethylene, hexamethylene, 1,12-dodecylene or 1,16-hexadecylene; a cycloalkylene group of 6 to about 20 carbon atoms, such as 1,3-cyclohexylene, 1,4-cyclohexylene, 2,3-norbornylene or 2,5(6)-norbornylene; a cycloalkylenebisalkylene group of 8 to about 20 carbon atoms, such as 1,4-cyclohexylenedimethylene or 1,4-cyclohexylenediethylene; an arylenebisalkylene group of 8 to about 20 carbon atoms, such as 1,4-phenylenediethylene; or an arylene group of 6 to about 12 carbon atoms, such as phenylene, tolylene or naphthylene; and

(II) an acid component which comprises:

(a) 8 to 30 mole percent of units derived from one or more ionic dicarboxylic acids, said units having the structures:

SO₃M

, and

-continued

$$SO_2$$
 $N \oplus M \oplus$
 SO_2
 CH_3

wherein M is ammonium (including tetraorganoammonium, such as tetramethylammonium or tetraethylammonium) or a monovalent metal, such as sodium, lithium or potassium; and

(b) 70 to 92 mole percent of recurring units derived from other diacids.

In a preferred embodiment of our invention, the recurring units derived from the other diacids comprise one or more of the following:

(A) 0 to 80 mole percent of diacids selected from the group consisting of:

(I) aliphatic dicarboxylic acids, said units having the structure:

wherein p is an integer of from 2 to 12;

(II) cycloaliphatic diacids, said units having the structures:

$$-\frac{0}{C}$$
 s 0 or 0

(III) aromatic diacids, said units having the structure:

(B) 0 to 60 mole percent of recurring units having the structure:

(C) 0 to 30 mole percent of recurring units derived from an alkylenebisamide, said units having the structure:

$$Z+CH_2)_{\overline{q}}Z$$

wherein each Z is iminocarbonyl or carbonylimino, and q is an integer of from 6 to 10.

A photographic assemblage in accordance with our 20 invention comprises a photographic element as disclosed above, and a dye image-receiving element comprising a support having thereon a dye image-receiving layer, said receiving element being adapted to be superposed on said photographic element after exposure 25 thereof.

A process for producing a photographic image in accordance with our invention comprises immersing an exposed photographic element, as described above, in a processing composition, and then bringing the photo- 30 graphic element into face-to-face contact with a dye image-receiving element as described above. The exposed photographic element can be immersed in the processing composition for periods of time ranging from 5 seconds to 30 seconds at temperatures from 15° 35 C. to 32° C. to effect development of each of the exposed silver halide emulsion layers. The photographic element is then laminated to the dye image-receiving element by passing the two elements together in face-toface contact through the nip of two rollers. The assem- 40 blage is then left laminated together for a period of time ranging from between 1 minute and 15 minutes. An imagewise distribution of dye image-providing material is thus formed as a function of development, and at least to provide the transfer image. The receiving element is then peeled apart from the photographic element. The image formed in the receiving element can either be a negative or a positive, depending upon whether or not the photosensitive emulsions employed in the donor 50 element are negative emulsions or direct-positive emulsions, and depending on whether positive-working or negative-working image-forming chemistry is employed.

Vinylidene chloride polymers useful in the practice 55 halide. of this invention include the following:

COMPOUND 1

Poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 14/79/7).

COMPOUND 2

Poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 10/85/5).

COMPOUND 3

Poly(monobutyl itaconate-co-vinylidene chloride) (weight ratio 9/91).

COMPOUND 4

Poly(methyl acrylate-co-vinylidene chloride-co-itaconic acid) (weight ratio 15/83/2).

The vinylidene chloride polymer layer may be coated at coverages ranging from 0.15 to 1.5 g/m². Generally, good results have been obtained at coverages ranging from about 0.25 to 0.75 g/m².

Ionic vinyl polymers useful in the practice of this ¹⁰ invention include the following:

COMPOUND 5

Poly(2-methacryloyloxyethyltrimethylammonium methosulfate-co-2-hydroxyethyl acrylate).

COMPOUND 6

Poly[N-(3-acrylamido-3,3-dimethylpropyl)-N,N,Ntrimethylammonium methosulfate-co-N-(2-hydroxyethylacrylamide)].

COMPOUND 7

Poly[N-(2-methacryloyloxyethyl)-N,N-dimethyl-Nbenzylammonium chloride-co-2-hydroxyethyl methacrylate].

COMPOUND 8

Poly[N-(2-hydroxy-3-methacryloyloxypropyl)-N,N,N-trimethylammonium chloride-co-2,3-dihydroxypropyl acrylatel.

COMPOUND 9

Poly[N-(2-methacryloyloxyethyl)-N,N,N-trimethylammonium-p-toluenesulfonate-co-2-hydroxyethyl acrylate].

The ionic vinyl polymeric layer may be coated at coverages ranging from 0.15 to 1.5 g/m². Generally, good results have been obtained at coverages ranging from about 0.25 to 0.75 g/m². The ionic polymer layer may also contain hydrophilic colloids, such as gelatin, if desired. In some embodiments of the invention, the ionic polymer may be mixed in with the overlying emulsion layer, if desired.

Generally, the ionic polyesters useful in the present a portion of it diffuses to the dye image-receiving layer 45 invention are formed by condensing a glycol component of one of more polyhydric alcohols with an acid component of at least two carboxylic acids, each containing at least two condensation sites. It is noted that amido groups can be used as linking groups, rather than ester groups. This modification is readily achieved by condensing in the presence of amino alcohols or diamines. The carboxylic acids can be condensed in the form of a free acid or in the form of a functional derivative, such as an anhydride, a lower alkyl ester or an acid

> Exemplary diols which are utilized in preparing the condensation polyesters useful in this invention include 1,4-bis(2-hydroxyethoxy)cyclohexane, 1,4-bis(2hydroxypropoxy)cyclohexane, 1,4-bis(2-hydroxybutox-60 y)cyclohexane, ethylene glycol, diethylene glycol, 1,3propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, neopentyl gly-2-ethyl-2-methyl-1,4-butanediol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, triethylene 65 glycol, tetraethylene glycol, 2,3-norbornanediol or 2,5(6)-norboranediol. The corresponding diamines can, if desired, be substituted for the diols in forming condensation copolymers useful in the present invention.

One or a mixture of diols and/or diamines can be used, also.

Ionic dicarboxylic acids in the above formula are disclosed in U.S. Pat. No. 3,546,180 of Caldwell et al, issued Dec. 8, 1970, and U.S. Pat. No. 3,929,489 of 5 Arcesi et al, issued Dec. 30, 1975, and in British Pat. No. 1,470,059, the disclosures of which are hereby incorporated by reference.

From about 70 to about 92 mole percent of the acid component of the polyesters useful in the present inven- 10 tion is derived from one or more other diacids or functional derivatives thereof. Exemplary of such diacids are aromatic dicarboxylic acids, such as phthalic acid, isophthalic acid or terephthalic acid, aliphatic dicarboxylic acids, such as malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic and other higher homolog dicarboxylic acids which may be aryl- or alkylsubstituted; cycloaliphatic dicarboxylic acids, such as 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 3,5-cyclohexenedicarboxylic acid, or 1,5-cyclohexa-1,3-dienedicarboxylic acid; lightsensitive ethylenically unsaturated dicarboxylic acids, such as p-phenylenebisacrylic acid, as disclosed in U.S. Pat. No. 3,929,489 of Arcesi et al.; alkylenebisamides, 25 such as N,N'-bis(4-carboxyphenyl)-1,8-octanediamide and 1,6-bis-(4-carboxyphenylcarbonylamino) hexane. Mixtures of these acids can be employed, if desired.

Ionic polyesters preferred in the practice of this invention include:

COMPOUND 10

Poly[1,4-cyclohexylenebis(oxyethylene)-co-1,4-cyclohexylenedimethylene (50:50) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisul-fonyldibenzoate (55:20:10:15)].

COMPOUND 11

Poly[1,4-cyclohexylenebis(oxyethylene) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisul-fonyldibenzoate (55:20:10:15)].

COMPOUND 12

Poly[1,4-cyclohexylenebis(oxyethylene) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,8-octylenebis(carbonylimino-4-benzoate)-co-3,3'-sodioiminodisul-fonyldibenzoate (55:20:10:15)].

COMPOUND 13

Poly[1,4-cyclohexylenebis(oxyethylene) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-phenoxy)-1,3-benzenedicarboxylate (15:55:30)].

COMPOUND 14

Poly[1,4-cyclohexylenebis(oxyethylene) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-phenoxy)-1,3-benzenedicarboxylate (45:40:15)].

COMPOUND 15

Poly[1,4-cyclohexylenebis(oxyethylene) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-phenoxy)-1,3-benzenedicarboxylate (60:10:30)].

COMPOUND 16

Poly[1,4-cyclohexylenebis(oxyethylene) sebacate-co-3,3'-(1,4-phenylene)bisacrylate (80:20)].

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COMPOUND 17

Poly[1,4-cyclohexylenebis(oxyethylene) terephthalate-co-1-methyl-1-cyclohexane-4,5-dicarboxylate-co-5-(N-potassio-p-tolylsulfonamidosulfonyl)-1,3-benzenedicarboxylate (10:70:20)].

The condensation polyesters described herein can be prepared by procedures well known in the art for making linear condensation polymers, particularly interfacial, solution or ester interchange procedures, the latter being preferred. Reaction times are a function of all other variables and, as such, are governed by the inherent viscosity desired for the resulting polymer.

When employing interfacial procedures, polymerization is carried out in suitable halogenated solvents, such as methylene chloride, chloroform, dichloroethane, propylene dichloride and the like. Reaction temperatures are governed by maintenance of a practical rate of reaction and the boiling point of the solvent, with a range of 10° C. to 40° C. being suitable.

Solution polymerization procedures can be carried out by condensing suitable acid halides, such as chlorides, of the dicarboxylic acids to be incorporated with the desired diols in a suitable solvent, such as phenylenebis(acrylic acid chlorides), hexamethylenebis(4-iminocarbonylbenzoic acid chlorides) or sodioiminodisulfonyldibenzoic acid chlorides, in the presence of a suitable acid acceptor, such as pyrdine, triethylamine or tripropylamine. The acid acceptor can be employed in excess to serve as the solvent.

The preferred mode of preparing the polyesters disclosed herein is the ester interchange procedure either by melt or powder process, and preferably by the melt process. The diols of the glycol component and the 35 carboxylates of the acid component are heated to a melt on an approximately equal molar basis and treated with a transesterification catalyst, such as alkali or alkaline earth metal carbonates, oxides, hydroxides, hydrides and alkoxides; or compounds of a Group IVB metal of the Periodic Table, such as tetraisopropyl orthotitanate, butyl titanate, organo-metallic halides and complex alkoxides such as NaHTi(OC₄H₉)₂. As a practical matter, it is frequently desirable to utilize an excess of up to about 80 molar percent of the glycol component in the 45 reaction mixture. Low boiling alcohols are removed by distillation during polymerization.

In general, it is desirable that the condensation copolymers described herein exhibit an inherent viscosity of from about 0.15 to about 0.90 and preferably from 0.2 to 0.8, as measured at 25° C. at a concentration of 0.25 grams per deciliter in a 1:1 mixture of phenol and chlorobenzene.

The ionic polyester layer may be coated at coverages ranging from 0.15 to 1.5 g/m². Generally, good results have been obtained at coverages ranging from about 0.25 to 0.75 g/m².

The dye image-providing material useful in our invention is either positive- or negative-working, and is either initially mobile or immobile in the photographic element during processing with an alkaline composition. Examples of initially mobile, positive-working dye image-providing materials useful in our invention are described in U.S. Pat. Nos. 2,983,606; 3,536,739; 3,705,184; 3,482,972; 2,756,142; 3,880,658 and 3,854,985.

65 Examples of negative-working dye image-providing materials useful in our invention include conventional couplers which react with oxidized aromatic primary amino color developing agents to produce or release a

dye such as those described, for example, in U.S. Pat. No. 3,227,550 and Canadian Pat. No. 602,607. In a preferred embodiment of our invention, the dye imageproviding material is a ballasted, redox-dye-releasing (RDR) compound. Such compounds are well known to 5 those skilled in the art and are, generally speaking, compounds which will react with oxidized or unoxidized developing agent or electron transfer agent to release a dye. Such nondiffusible RDR's include positive-working compounds, as described in U.S. Pat. Nos. 10 3,980,479; 4,139,379; 4,139,389; 4,199,354 and 4,199,355. Such nondiffusible RDR's also include negative-working compounds, as described in U.S. Pat. Nos. 3,728,113 of Becker et al; 3,725,062 of Anderson and Lum; 3,698,897 of Gompt and Lum; 3,628,952 to Puschel et al; 15 3,443,939 and 3,443,940 of Bloom et al; 4,053,312 of Fleckenstein; 4,076,529 of Fleckenstein et al; 4,055,428 of Koyama et al; German Pat. Nos. 2,505,248 and 2,729,820; Research Disclosure 15157, November, 1976 and Research Disclosure 15654, April, 1977.

In a preferred embodiment of our invention, the dyereleasers such as those of the Fleckenstein et al patent referred to above are employed. Such compounds are ballasted sulfonamido compounds which are alkalicleavable upon oxidation to release a diffusible dye from the nucleus and have the formula:

Y (Ballast)
$$_{n-1}$$
NHSO₂—Col

wherein

(a) Col is a dye or dye precursor moiety;

(b) Ballast is an organic ballasting radical of such molecular size and configuration (e.g., simple organic groups or polymeric groups) as to render the compound nondiffusible in the photosensitive element during development in an alkaline processing composition;

(c) G is OR₈ or NHR₉ wherein R₈ is hydrogen or a hydrolyzable moiety and R₉ is hydrogen or a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms, such as methyl, ethyl, hydroxyethyl, propyl, ⁴⁵ butyl, secondary butyl, tertiary butyl, cyclopropyl, 4-chlorobutyl, cyclobutyl, 4-nitroamyl, hexyl, cyclohexyl, octyl, decyl, octadecyl, docosyl, benzyl or phenethyl (when R₉ is an alkyl group of greater than 6 carbon atoms, it can serve as a partial or sole Ballast ⁵⁰ group);

(d) Y represents the atoms necessary to complete a benzene nucleus, a naphthalene nucleus or a 5- to 7-membered heterocyclic ring such as pyrazolone or pyrimidine; and

(e) n is a positive integer or 1 to 2 and is 2 when G is OR₈ or when R₉ is a hydrogen or an alkyl group of less than 8 carbon atoms.

For further details concerning the above-described sulfonamido compounds and specific examples of same, 60 reference is made to the above-mentioned Fleckenstein et al U.S. Pat. No. 4,076,529 referred to above.

In another preferred embodiment of our invention, positive-working, nondiffusible RDR's of the type disclosed in U.S. Pat. Nos. 4,139,379 and 4,139,389 are 65 employed. In this embodiment, an immobile compound is employed which as incorporated in a photographic element is incapable of releasing a diffusible dye. How-

ever, during photographic processing under alkaline conditions, the compound is capable of accepting at least one electron (i.e., being reduced) and thereafter releases a diffusible dye. These immobile compounds are ballasted electron accepting nucleophilic displacement (BEND) compounds.

BEND compounds are ballasted compounds that undergo intramolecular nucleophilic displacement to release a diffusible moiety, such as a dye. They contain a precursor for a nucleophilic group which accepts at least one electron before the compound can undergo intramolecular nucleophilic displacement. In a preferred embodiment described in U.S. Pat. No. 4,139,379, the BEND compounds are processed in silver halide photographic elements with an electron transfer agent and an electron donor (i.e., a reducing agent) which provides the necessary electrons to enable the compound to be reduced to a form which will undergo intramolecular nucleophilic displacement. In this embodiment, the BEND compound reacts with the electron donor to provide a nucleophilic group which in turn enters into an intramolecular nucleophilic displacement reaction to displace a diffusible dye from the compound. However, where there are no electrons transferred to the electron accepting nucleophilic precursor, it remains incapable of displacing the diffusible dye. An imagewise distribution of electron donor is obtained in the photographic element by oxidizing the electron donor in an imagewise pattern before it has reacted with the BEND compound, leaving a distribution of unoxidized electron donor available to transfer electrons to the BEND compound. An imagewise distribution of oxidized electron donor is provided by reaction of the 35 electron donor with an imagewise distribution of oxidized electron transfer agent, which in turn is obtained by reaction of a uniform distribution of electron transfer agent with an imagewise pattern of developable silver halide.

Thus, in processing an imagewise-exposed photographic element containing a BEND compound, the following reactions lead to an imagewise distribution of diffusible dye: In exposed areas, developable silver halide is developed by electron transfer agent, thereby providing oxidized electron transfer agent which reacts with and oxidizes electron donor, thus preventing it from reacting with BEND compound. In unexposed areas, there is no developable silver halide and, hence, neither electron transfer agent nor electron donor are oxidized. Thus, electron donor reacts with BEND compound to release diffusible dye.

The film unit or assemblage of the present invention is used to produce positive images in single or multicolors. In a three-color system, each silver halide emulsion 55 layer of the film assembly will have associated therewith a dye image-providing material which possesses a predominant spectral absorption within the region of the visible spectrum to which said silver halide emulsion is sensitive, i.e., the blue-sensitive silver halide emulsion layer will have a yellow dye image-providing material associated therewith, the green-sensitive silver halide emulsion layer will have a magenta dye imageproviding material associated therewith and the redsensitive silver halide emulsion layer will have a cyan dye image-providing material associated therewith. The dye image-providing material associated with each silver halide emulsion layer is contained either in the silver halide emulsion layer itself or in a layer contiguous

to the silver halide emulsion layer, i.e., the dye imageproviding material can be coated in a separate layer underneath the silver halide emulsion layer with respect to the exposure direction.

The concentration of the dye image-providing material that is employed in the present invention can be varied over a wide range, depending upon the particular compound employed and the results desired. For example, the dye image-providing material coated in a layer at a concentration of 0.1 to 3 g/m² has been found 10 to be useful. The dye image-providing material is dispersed in a hydrophilic film forming natural material or synthetic polymer, such as gelatin or polyvinyl alcohol, which is adapted to be permeated by aqueous alkaline processing composition.

A variety of silver halide developing agents are useful in this invention. Specific examples of developers or electron transfer agents (ETA) compounds useful in this invention include hydroquinone compounds, such as hydroquinone, 2,5-dichlorohydroquinone or chlorohydroquinone; aminophenol compounds, such as 4-aminophenol, N-methylaminophenol, N,N-dimethylaminophenol, 3-methyl-4-aminophenol or 3,5dibromoaminophenol; catechol compounds, such as catechol, 4-cyclohexylcatechol, 3-methoxycatechol or 25 4-(N-octadecylamino)catechol; phenylenediamine compounds, such as N,N-diethyl-p-phenylenediamine, 3methyl-N,N-diethyl-p-phenylenediamine, 3-methoxy-N-ethyl-N-ethoxy-p-phenylenediamine or N,N,N',N'tetramethyl-p-phenylenediamine. In highly preferred 30 embodiments, the ETA is a 3-pyrazolidinone compound, such as 1-phenyl-3-pyrazolidinone (Phenidone), 1-phenyl-4,4-dimethyl-3-pyrazolidinone (Dimezone), 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone, 4-hydroxymethyl-4-methyl-1-p-tolyl-3-pyrazolidinone, 4-hydroxymethyl-4-methyl-1-(3,4-dimethylphenyl)-3pyrazolidinone, 1-m-tolyl-3-pyrazolidinone, 1-p-tolyl-3pyrazolidinone, 1-phenyl-4-methyl-3-pyrazolidinone, 1-phenyl-5-methyl-3-pyrazolidinone, 1-phenyl-4,4-1,4-dimethyl-3- 40 dihydroxymethyl-3-pyrazolidinone, pyrazolidinone, 4-methyl-3-pyrazolidinone, 4,4-dimeth-1-(3-chlorophenyl)-4-methyl-3yl-3-pyrazolidinone, pyrazolidinone, 1-(4-chlorophenyl)-4-methyl-3pyrazolidinone, 1-(3-chlorophenyl)-3-pyrazolidinone, 1-(4-chlorophenyl)-3-pyrazolidinone, 1-(4-tolyl)-4-45 methyl-3-pyrazolidinone, 1-(2-tolyl)-4-methyl-3pyrazolidinone, 1-(4-tolyl)-3-pyrazolidinone, 1-(3tolyl)-3-pyrazolidinone, 1-(3-tolyl)-4,4-dimethyl-3pyrazolidinone, 1-(2-trifluoroethyl)-4,4-dimethyl-3pyrazolidinone or 5-methyl-3-pyrazolidinone. A combi- 50 nation of different ETA's, such as those disclosed in U.S. Pat. No. 3,039,869, can also be employed. While such developing agents may be employed in the liquid processing comosition, we have obtained good results when the ETA is incorporated in a layer or layers of the 55 photographic element or receving element to be activated by the alkaline processing composition, such as in the silver halide emulsion layers, the dye image-providing material layers, interlayers, or the image-receiving layer.

In using dye image-providing materials in the invention which produce diffusible dye images as a function of development, either conventional negative-working or direct-positive silver halide emulsions are employed. If the silver halide emulsion employed is a direct-positive silver halide emulsion, such as an internal image emulsion designed for use in the internal image reversal process, or a fogged, direct-positive emulsion such as a

solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained on the dye image-receiving layer by using ballasted, redox, dyereleasers. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed photosensitive silver halide emulsion layers. The developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct-positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed areas of the direct-positive silver halide emulsion layers. The oxidized developing agent then cross-oxidizes the dye-releasing compounds and the oxidized form of the compounds then undergoes a base-catalyzed reaction to release the dyes imagewise as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distributions of diffusible dyes diffuse to the image-receiving layer to form a positive image of the original subject.

Internal image silver halide emulsions useful in this invention are described more fully in the November, 1976 edition of *Research Disclosure*, pages 76 through 79, the disclosure of which is hereby incorporated by reference.

The various silver halide emulsion layers of a color film assembly employed in this invention are disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers. If desired, a yellow dye layer or a yellow colloidal silver layer can be present between the blue-sensitive and green-sensitive silver halide emulsion layers for absorbing or filtering blue radiation that is transmitted through the blue-sensitive layer. If desired, the selectively sensitized silver halide emulsion layers can be disposed in a different order, e.g., the blue-sensitive layer first with respect to the exposure side, followed by the red-sensitive and green-sensitive layers.

Generally speaking, except where noted otherwise, the silver halide emulsion layers employed in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye image-providing materials are dispersed in an aqueous alkaline solution-permeable polymeric binder, such as gelatin, as a separate layer about 0.2 to 7 microns in thickness; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 0.2 to 5 microns in thickness. Of course, these thicknesses are approximate only and can be modified according to the product desired.

Any material is useful as the dye image-receiving layer in this invention, as long as the desired function of mordanting or otherwise fixing the dye images is obtained. The particular material chosen will, of course, depend upon the dye to be mordanted. Suitable materials are disclosed on pages 80 through 82 of the November, 1976 edition of *Research Disclosure*, the disclosure of which is hereby incorporated by reference.

Use of a neutralizing layer in the photographic element of this invention will usually increase the stability of the transferred image. Generally, the neutralizing material will effect a reduction in the pH of the image layer from about 13 or 14 to at least 11, and preferably 5 to 8 within 3 to 4 minutes after imbibition. Suitable materials and their functions are disclosed on pages 22

and 23 of the July, 1974 edition of Research Disclosure, and pages 35 through 37 of the July, 1975 edition of Research Disclosure, the disclosures of which are hereby incorporated by reference.

One or more timing or inert spacer layers can be 5 employed in the practice of this invention over the neutralizing layer which "times" or controls the pH reduction as a function of the rate at which the alkaline composition diffuses through the inert spacer layer or layers. Examples of such timing layers and their functions are disclosed in the *Research Disclosure* articles mentioned in the paragraph above concerning pH-lowering layers.

The above-described acid layers and timing layers together constitute process control layers for "shutting down" the system after the required development has taken place. These process control layers are located in the donor element.

as gelatin, in the photographic elements of the invention in an alkaline medium and preferably when processed in a medium having a pH of 11 or greater. The same meaning is to be attached to the term "immobile". The term "diffusible" as applied to the materials of this invention down.

The alkaline processing or activating composition employed in this invention is the conventional aqueous 20 solution of an alkaline material, e.g., alkali metal hydroxides or carbonates such as sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 11. In some embodiments of the invention, the processing composition may 25 contain a developing agent. Suitable materials and addenda frequently added to such compositions are disclosed on pages 79 and 80 of the November, 1976 edition of *Research Disclosure*, the disclosure of which is hereby incorporated by reference.

The supports for the photographic element and receiving element used in this invention can be any material, as long as it does not deleteriously affect the photographic properties and is dimensionally stable. Typical flexible sheet materials are described on page 85 of the 35 November, 1976 edition of *Research Disclosure*, the disclosure of which is hereby incorporated by reference.

While the invention has been described with reference to layers of silver halide emulsions and dye image- 40 providing materials, dotwise coating, such as would be obtained using a gravure printing technique, could also be employed. In this technique, small dots of blue-, green- and red-sensitive emulsions have associated therewith, respectively, dots of yellow, magenta and 45 cyan color-providing substances. After development, the transferred dyes would tend to fuse together into a continuous tone.

The silver halide emulsions useful in this invention, both negative-working and direct-positive ones, are 50 well known to those skilled in the art and are described in Research Disclosure, Volume 176, December, 1978, Item 17643, pages 22 and 23, "Emulsion preparation and types"; they are usually chemically and spectrally sensitized as described on page 23, "Chemical sensitization", 55 and "Spectral sensitization and desensitization", of the above article; they are optionally protected against the production of fog and stabilized against loss of sensitivity during keeping by employing the materials described on pages 24 and 25, "Antifoggants and stabiliz- 60 ers", of the above article; they usually contain hardeners and coating aids as described on page 26, "Hardeners", and pages 26 and 27, "Coating aids", of the above article; they and other layers in the photographic elements used in this invention usually contain plasticizers, 65 vehicles and filter dyes described on page 27, "Plasticizers and lubricants"; page 26, "Vehicles and vehicle extenders"; and pages 25 and 26, "Absorbing and scat-

tering materials", of the above article; they and other layers in the photographic elements used in this invention can contain addenda which are incorporated by using the procedures described on page 27, "Methods of addition", of the above article; and they are usually coated and dried by using the various techniques described on pages 27 and 28, "Coating and drying procedures", of the above article, the disclosures of which are hereby incorporated by reference.

The term "nondiffusing" used herein has the meaning commonly applied to the term in photography and denotes materials that for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, in the photographic elements of the invention in an alkaline medium and preferably when processed in a medium having a pH of 11 or greater. The same meaning is to be attached to the term "immobile". The term "diffusible" as applied to the materials of this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the photographic elements in an alkaline medium. "Mobile" has the same meaning as "diffusible".

The term "associated therewith" as used herein is intended to mean that the materials can be in either the same or different layers, so long as the materials are accessible to one another.

The following examples are provided to further illustrate the invention.

EXAMPLE 1

Photosensitive (donor) elements are prepared by coating the following layers in the order recited on an opaque poly(ethylene terephthalate) film support;

(1) Polymeric acid layer

(2) Timing layer

- (3) Primer layer of poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 13/73/14) (0.37 g/m²)
- (4) Primer layer (see Table)
- (5) Cyan redox dye-releaser layer
- (6) Red-sensitive, negative-working, silver halide emulsion layer
- (7) Interlayer
- (8) Magenta redox dye-releaser layer
- (9) Green-sensitive, negative-working, silver halide emulsion layer
- (10) Interlayer
- (11) Yellow redox dye-releaser layer
- (12) Blue-sensitive, negative-working, silver halide emulsion layer
 - (13) Matte overcoat layer

The polymeric acid layer and timing layer are similar to those described in the examples of Abel U.S. Application Ser. No. 948,062, filed Oct. 2, 1978. The redox dye-releasers are similar to those described in *Research Disclosure* No. 18268, Volume 182, July 1979, pages 329 through 331. The silver halide emulsion layers are conventional negative-working, 0.25 to 0.65 μ silver chloride emulsions. The matte overcoat layer comprises gelatin (0.89 g/m²), methacrylate beads (2-4 μ , 0.017 g/m²), Ludox AM TM silica (particle size about 0.2 μ , 0.45 g/m²) and 2,5-didodecylhydroquinone (0.38 g/m²). The total gelatin coverage in layers 3 to 11 is 8.8 g/m², hardened with 0.75 percent bis(vinylsulfonyl)methyl ether.

A dye image-receiving element was then prepared by coating the following layers in the order recited on an opaque paper support:

- (1) Dye image-receiving layer containing 0.16 g/m² 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone and 3.2 g/m² of poly(1-vinylimidazole) quaternized to 10 percent with 2-hydroxyethyl chloride. This mordant forms no part of our invention and is the subject 5 of U.S. Application Ser. No. 875,464, filed Feb. 6, 1978 by Hollister.
- (2) Interlayer of gelatin (0.86 g/m²) and ultraviolet absorber 2-(2-hydroxy-3,5-di-t-amylphenyl) benzotriazole (0.54 g/m^2) .
- (3) Overcoat of gelatin (0.65 g/m²).

The total amount of gelatin in these layers was 2.6 g/m², hardened with formaldehyde.

An activator solution was prepared containing:

0.6 N
3.0 g/l
2.0 g/l
2.0 g/l

Samples of the above donor elements were flashed to maximum density, soaked in the activator solution above contained in a shallow-tray processor for 15 seconds at 28° C., and then laminated between nip rollers 25 to dry samples of the receiving element. After 10 minutes, the donor and receiver were pulled apart. The extent of areas of emulsion from the donor which have transferred to the receiver is estimated visually as follows:

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	IADLUI		
Primer Layer 4	Con- centration (g/m ²)	Percent of Emulsion Transferred to Receiver	
Compound 6*	0.45	5	35
Gelatin (control)*	1.6	100	
Compound 6 mixed	0.45	Edge transfer only	
with gelatin*	1.6		
None (control)		95	
Compound 6	0.45	5	
Gelatin (control)	1.6	100	40

^{*}Layers 4, 5 and 6 were combined

The results indicate that use of Compound 6, according to the invention, by itself or with gelatin in a primer layer or combined with an emulsion layer containing a 45 redox dye-releaser materially improves wet adhesion and reduces emulsion transfer to the receiver.

EXAMPLE 2

Donors similar to those of Example 1 are prepared, 50 except that layers 5 and 6 are combined, and layers 7 through 12 are replaced by gelatin. The total gelatin composition of layers 5 through 13 is 8.4 g/m², hardened with 0.75 percent bis(vinylsulfonyl)methyl ether.

The same evaluation procedure is used as in Example 55 1 with the materials used in primer layer 4 identified below. The longest lamination time at 29.5° C. for which no portions of the emulsion layer transfers to the receiver is recorded as follows:

TADIEII

- 	1 A	BLE II	
Primer Layer 4	Concen- tration (g/m²)	Maximum Time With No Appreciable Portions of Emulsion Layer Transferring to Receiver When Peeled Apart	— 65
Gelatin (control)	0.54	Less than 3 minutes	0.7
Compound 13 mixed	0.54	5 minutes	
with gelatin	0.54		
Compound 13	0.54	Greater than or equal to	

TABLE II-continued

Primer Layer 4	Concen- tration (g/m ²)	Maximum Time With No Appreciable Portions of Emulsion Layer Transferring to Receiver When Peeled Apart
None (control)		10 minutes Less than 3 minutes

The results indicate that use of Compound 13 with gelatin or by itself as a primer layer materially improves wet adhesion and reduces emulsion transfer to the receiver.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

- 1. In a photographic element comprising a support having thereon, in order, a neutralizing layer, a timing layer and at least one photosensitive silver halide emulsion layer having associated therewith a dye imageproviding material,
 - the improvement wherein a layer of a vinylidene chloride polymer is present between said timing layer and said emulsion layer, and a co-extensive polymeric primer layer is present between said vinylidene chloride polymeric layer and said silver halide emulsion layer, said primer layer comprising:
 - (A) an ionic vinyl polymer comprising 10 to 30 weight percent of recurring units which conform to the structure:

$$\begin{array}{cccc}
R \\
| & & \\
CH_2-C+ & & R^2 \\
| & & & \\
COGR^1-N^{\oplus}-R^3 & & X^{\ominus} \\
| & & & \\
R^4
\end{array}$$

and 70 to 90 weight percent of recurring units which conform to the structure:

$$R$$
 $|$
 $+CH_2-C+$
 $|$
 $COGR^{\dagger}OH$

wherein:

60

each R is independently hydrogen or methyl; each R1 is independently a straight or branched chain alkylene group of 1 to about 6 carbon atoms;

R², R³ and R⁴ are each an alkyl group of 1 to about 4 carbon atoms;

each G is independently oxygen or NH; and X – is an acid anion; or

- (B) a ionic polyester comprising recurring units of:
 - (I) a diol component which comprises: (a) at least 50 mole percent of units derived from diols having the structures:

60

65

$$-O+OCH_2CH_2+$$
 S $-(OCH_2CH_2+)_{\overline{n}}O-$ (i)

wherein n is an integer of from 1 to 4; and

- (ii) $O+R^6O+m$, wherein m is an integer of from 2 to 4, and R^6 is an alkylene group of 2 to about 4 carbon atoms; and
- (b) 0 to 50 mole percent of units derived from ¹⁵ one or more diols having the structure:

$$-O-R^{7}-O-$$

wherein R⁷ is an alkylene group of up to about
16 carbon atoms, a cycloalkylene group of 6
to about 20 carbon atoms, a cycloalk25
ylenebisalkylene group of 8 to about 20
carbon atoms, an arylenebisalkylene group
of 8 to about 20 carbon atoms, or an arylene
30
group of 6 to about 12 carbon atoms; and
(II) an acid component which comprises:

(a) 8 to 30 mole percent of units derived from one or more ionic dicarboxylic acids, said units having the structures:

 SO_3M

, and

wherein M is ammonium or a monovalent metal; and

(b) 70 to 92 mole percent of recurring units derived from other diacids.

 CH_3

- 2. The photographic element of claim 1 wherein said recurring units derived from said other diacids comprise one or more of the following:
 - (A) 0 to 80 mole percent of diacids selected from the group consisting of:
 - (I) aliphatic dicarboxylic acids, said units having the structure:

wherein p is an integer of from 2 to 12; (II) cycloaliphatic diacids, said units having the structures:

(III) aromatic diacids, said units having the structure:

(B) 0 to 60 mole percent of recurring units having the structure:

(C) 0 to 30 mole percent of recurring units derived from an alkylenebisamide, said unit having the structure:

$$Z+CH_2$$

wherein each Z is iminocarbonyl or carbonylimino, and q is an integer of from 6 to 10.

- 3. The photographic element of claim 1 wherein said primer layer comprises poly(2-methacryloyloxyethyl-trimethylammonium methosulfate-co-2-hydroxyethyl 15 acrylate) (weight ratio 20/80).
- 4. The photographic element of claim 1 wherein said vinylidene chloride polymeric layer comprises poly(a-crylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 14/79/7).
- 5. The photographic element of claim 1 wherein said primer layer comprises poly[1,4-cyclohexylenebis(oxyethylene)-co-1,4-cyclohexylenedimethylene (50:50) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)];

poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-

3,3'-(1,4-phenylene)bisacrylate-co-1,8octylenebis(carbonylimino-4-benzoate)-co-3,3'sodioiminodisulfonyldibenzoate (55:20:10:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-35

poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-phenoxy)-1,3-benzenedicarboxylate (15:55:30)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-

3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-phenoxy)-1,3-benzenedicarboxylate (45:40:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfo-

phenoxy)-1,3-benzenedicarboxylate (60:10:30)]; poly[1,4-cyclohexylenebis(oxyethylene)sebacate-co-3,3'-(1,4-phenylene)bisacrylate (80:20)]; or

poly[1,4-cyclohexylenebis(oxyethylene)terephthalate-co-1-methyl-1-cyclohexane-4,5-dicarboxylateco-5-(N-potassio-p-tolylsulfonamidosulfonyl)-1,3benzenedicarboxylate (10:70:20)].

6. The photographic element of claim 1 wherein said 50 dye image-providing material is a ballasted, redox dye-releaser.

7. The photographic element of claim 1 wherein said dye image-providing material is a ballasted sulfonamido compound which is alkali-cleavable upon oxidation to 55 release a diffusible color-providing moiety, said compound having the formula:

$$G$$
(Ballast)_{n-1}

NHSO₂—Col

60

wherein:

(a) Col is a dye or dye precursor moiety;

- (b) Ballast is an organic ballasting radical of such molecular size and configuration as to render said compound nondiffusible in the photosensitive element during development in an alkaline processing composition;
- (c) G is OR₈ or NHR₉ wherein R₈ is hydrogen or a hydrolyzable moiety and R₉ is hydrogen or an alkyl group of 1 to 22 carbon atoms;
- (d) Y represents the atoms necessary to complete a benzene nucleus, a naphthalene nucleus or a 5- to 7-membered heterocyclic ring; and
- (e) n is a positive integer of 1 to 2 and is 2 when G is OR₈ or when R₉ is a hydrogen or an alkyl group of less than 8 carbon atoms.
- 8. The photographic element of claim 7 wherein G is OH, n is 2 and Y is a naphthalene nucleus.
- 9. The photographic element of claim 1 wherein said silver halide emulsion is a direct-positive silver halide emulsion.
- 10. The photographic element of claim 1 wherein said dye image-providing material is a ballasted, electron-accepting nucleophilic displacement compound.
- 11. In a photographic element comprising a support having thereon, in order, a neutralizing layer, a timing layer, a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material,

the improvement wherein a layer of a vinylidene chloride polymer is present between said timing layer and said red-sensitive silver halide emulsion layer, and a coextensive polymeric primer layer is present between said vinylidene chloride polymeric layer and said red-sensitive silver halide emulsion layer, said primer layer comprising:

(A) an ionic vinyl polymer comprising 10 to 30 weight percent of recurring units which conform to the structure:

$$\begin{array}{ccc}
R & & \\
| & & \\
CH_2-C+ & & R^2 \\
| & & & \\
COGR^1-N^{\oplus}-R^3 & X^{\ominus} \\
| & & & \\
R^4
\end{array}$$

and 70 to 90 weight percent of recurring units which conform to the structure:

wherein:

40

each R is independently hydrogen or methyl; each R¹ is independently a straight or branched chain alkylene group of 1 to about 6 carbon atoms;

- R², R³ and R⁴ are each an alkyl group of 1 to about 4 carbon atoms;
- each G is independently oxygen or NH; and $X\Theta$ is an acid anion; or
- (B) a ionic polyester comprising recurring units of:(I) a diol component which comprises:

(a) at least 50 mole percent of units derived from diols having the structures:

$$-O+CH2CH2O)_{\overline{n}}$$
S
$$-(OCH2CH2)_{\overline{n}}O-$$
10

wherein n is an integer of from 1 to 4; and

- (ii) $O+R^6O+_m$, wherein m is an integer of from 2 to 4, and R^6 is an alkylene group of 2 to about 4 carbon atoms; and
- (b) 0 to 50 mole percent of units derived from one or more diols having the structure:

$$-O-R^7-O-$$

wherein R⁷ is an alkylene group of up to about
16 carbon atoms, a cycloalkylene group of 6 25
to about 20 carbon atoms, a cycloalkylene bisalkylene group of 8 to about 20
carbon atoms, an arylenebisalkylene group
of 8 to about 20 carbon atoms, or an arylene
group of 6 to about 12 carbon atoms; and
(II) an acid component which comprises:

(a) 8 to 30 mole percent of units derived from 35 one or more ionic dicarboxylic acids, said units having the structures:

SO₃M

, and

wherein M is ammonium or a monovalent metal; and

- (b) 70 to 92 mole percent of recurring units derived from other diacids.
- 12. In a photographic assemblage comprising:
- (a) a photographic element comprising a support having thereon, in order, a neutralizing layer, a timing layer and at least one photosensitive silver halide emulsion layer having associated therewith a dye image-providing material; and
- (b) a dye image-receiving element comprising a support having thereon a dye image-receiving layer, said receiving element being adapted to be superposed on said photographic element after exposure thereof;

the improvement wherein a layer of a vinylidene chloride polymer is present between said timing layer and said emulsion layer, and a coextensive polymeric primer layer is present between said vinylidene chloride polymeric layer and said silver halide emulsion layer, said primer layer comprising:

(A) an ionic vinyl polymer comprising 10 to 30 weight percent of recurring units which conform to the structure:

$$\begin{array}{ccc}
R \\
| \\
CH_2-C+ & R^2 \\
| & | \\
COGR^1-N^{\oplus}-R^3 & X^{\ominus}
\end{array}$$

and 70 to 90 weight percent of recurring units which conform to the structure:

$$+CH_2-C+$$
 $+CH_2-C+$
 $COGR^1OH$

wherein:

65

each R is independently hydrogen of methyl; each R¹ is independently a straight or branched chain alkylene group of 1 to about 6 carbon atoms;

R², R³ and R⁴ are each an alkyl group of 1 to about 4 carbon atoms;

55

-continued

each G is independently oxygen or NH; and X- is an acid anion; or

- (B) an ionic polyester comprising recurring units of:
 - (I) a diol component which comprises:
 - (a) at least 50 mole percent of units derived from diols having the structures:

$$-O+CH_2CH_2O)_{H}$$
 S $-(OCH_2CH_2)_{H}O-$

wherein n is an integer of from 1 to 4; and (ii) $O + R^6O - m$, wherein m is an integer of from 2 to 4, and R⁶ is an alkylene group of 2 to about 4 carbon atoms; and

(b) 0 to 50 mole percent of units derived from one or more diols having the structure:

$$-0-R^{7}-0-$$

wherein R⁷ is an alkylene group of up to about 16 carbon atoms, a cycloalkylene group of 6 to about 20 carbon atoms, a cycloalkylenebisalkylene group of 8 to about 20 30 carbon atoms, an arylenebisalkylene group of 8 to about 20 carbon atoms, or an arylene group of 6 to about 12 carbon atoms; and

(II) an acid component which comprises:

(a) 8 to 30 mole percent of units derived from one or more ionic dicarboxylic acids, said units having the structures:

 SO_3M

, and

$$SO_2$$
 SO_2
 SO_2
 CH_3

wherein M is ammonium or a monovalent metal; and

- (b) 70 to 92 mole percent of recurring units derived from other diacids.
- 13. The photographic assemblage of claim 12 wherein said recurring units derived from said other diacids comprise one or more of the following:
 - (A) 0 to 80 mole percent of diacids selected from the group consisting of:
 - (I) aliphatic dicarboxylic acids, said units having the structure:

wherein p is an integer of from 2 to 12;

(II) cycloaliphatic diacids, said units having the structures:

(III) aromatic diacids, said units having the structure:

60 (B) 0 to 60 mole percent of recurring units having the structure:

(C) 0 to 30 mole percent of recurring units derived from an alkylenebisamide, said units having the structure:

$$Z+CH_2$$

wherein each Z is iminocarbonyl or carbonylimino, and q is an integer of from 6 to 10.

14. The photographic assemblage of claim 12 wherein said primer layer comprises poly(2-methacryloyloxyethyltrimethylammonium methosulfate-co-2-hydrox-15 yethyl acrylate) (weight ratio 20/80).

15. The photographic assemblage of claim 12 wherein said vinylidene chloride polymeric layer comprises poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 14/79/7).

16. The photographic assemblage of claim 12 wherein said primer layer comprises poly[1,4-cyclohexylenebis-(oxyethylene)-co-1,4-cyclohexylenedimethylene (50:50) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)];

25 oiminodisulfonyldibenzoate (55:20:10:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,8octylenebis(carbonylimino-4-benzoate)-co-3,3'sodioiminodisulfonyldibenzoate (55:20:10:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (15:55:30)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (45:40:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (60:10:30)]; poly[1,4-cyclohexylenebis(oxyethylene)sebacate-co-3,3'-(1,4-phenylene)bisacrylate (80:20)]; or poly[1,4-cyclohexylenebis(oxyethylene)terephthalate-co-1-methyl-1-cyclohexene-4,5-dicarboxylateco-5-(N-potassio-p-tolylsulfonamidosulfonyl)-1,3benzenedicarboxylate (10:70:20)].

17. In a process for producing a photographic image wherein an exposed photographic element is immersed in a processing solution, said photographic element comprising a support having thereon, in order, a neutralizing layer, a timing layer and at least one photosensitive silver halide emulsion layer having associated therewith a dye image-providing material, said photographic element then being brought into face-to-face contact for a period of time with a dye image-receiving element, said receiving element comprising a support having thereon a dye image-receiving layer, said receiving element then being separated from said photographic element,

the improvement which comprises preventing transfer of portions of said emulsion layer to said dye image-receiving element during processing by means of a layer of a vinylidene chloride 65 polymer located between said timing layer and said emulsion layer, and a coextensive polymeric primer layer located between said vinylidene

chloride polymeric layer and said silver halide emulsion layer, said primer layer comprising:

(A) an ionic vinyl polymer comprising 10 to 30 weight percent of recurring units which conform to the structure:

$$\begin{array}{cccc}
R \\
| \\
CH_2-C \rightarrow & R^2 \\
| & | \\
COGR^1-N^{\oplus}-R^3 & X^{\ominus} \\
| & & | \\
R^4
\end{array}$$

and 70 to 90 weight percent of recurring units which conform to the structure:

$$R$$
 $|$
 $+CH_2-C+$
 $|$
 $COGR^1OH$

wherein:

each R is independently hydrogen or methyl; each R¹ is independently a straight or branched chain alkylene group of 1 to about 6 carbon atoms;

R², R³ and R⁴ are each an alkyl group of 1 to about 4 carbon atoms;

each G is independently oxygen or NH; and $X\Theta$ is an acid anion; or

(B) a ionic polyester comprising recurring units of:(I) a diol component which comprises:

(a) at least 50 mole percent of units derived from diols having the structures:

$$-O+CH_2CH_2O)_{\overline{n}}$$
 S $-(OCH_2CH_2)_{\overline{n}}O-$

wherein n is an integer of from 1 to 4; and (ii) $O+R^6O+m$, wherein m is an integer of from 2 to 4, and R^6 is an alkylene group of 2 to about 4 carbon atoms; and

(b) 0 to 50 mole percent of units derived from one or more diols having the structure:

wherein R⁷ is an alkylene group of up to about 16 carbon atoms, a cycloalkylene group of 6 to about 20 carbon atoms, a cycloalkylenebisalkylene group of 8 to about 20 carbon atoms, an arylenebisalkylene group of 8 to about 20 carbon atoms, or an arylene group of 6 to about 12 carbon atoms; and

(II) an acid component which comprises:(a) 8 to 30 mole percent of units derived from one or more ionic dicarboxylic acids, said units

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wherein M is ammonium or a monovalent metal; and

- (b) 70 to 92 mole percent of recurring units derived from other diacids.
- 18. The process of claim 17 wherein said recurring units derived from said other diacids comprise one or more of the following:
 - (A) 0 to 80 mole percent of diacids selected from the 50 group consisting of:
 - (I) aliphatic dicarboxylic acids, said units having the structure:

wherein p is an integer of from 2 to 12; (II) cycloaliphatic diacids, said units having the structures:

(III) aromatic diacids, said units having the structure:

(B) 0 to 60 mole percent of recurring units having the structure:

(C) 0 to 30 mole percent of recurring units derived from an alkylenebisamide, said units having the structure:

$$30 \qquad \bigcup_{C} Z + CH_2 + \overline{q}Z$$

wherein each Z is iminocarbonyl or carbonylimino, and q is an integer of from 6 to 10.

19. The process of claim 17 wherein said primer layer comprises poly(2-methacryloyloxyethyltrimethylammonium methosulfate-co-2-hydroxyethyl acrylate) (weight ratio 20/80).

20. The process of claim 17 wherein said vinylidene chloride polymer layer comprises poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (weight ratio 14/79/7).

21. The process of claim 17 wherein said primer layer comprises poly[1,4-cyclohexylenebis(oxyethylene)-co-1,4-cyclohexylenedimethylene (50:50) succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)];

poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,6-hexylenebis-(iminocarbonyl-4-benzoate)-co-3,3'-sodioiminodisulfonyldibenzoate (55:20:10:15)];

poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-1,8octylenebis(carbonylimino-4-benzoate)-co-3,3'sodioiminodisulfonyldibenzoate (55:20:10:15)];

poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (15:55:30)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-

3,3'-(1,4-phenylene)bisacrylate-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (45:40:15)]; poly[1,4-cyclohexylenebis(oxyethylene)succinate-co-3,3'-(1,4-phenylene)bisacrylae-co-5-(4-sodiosulfophenoxy)-1,3-benzenedicarboxylate (60:10:30)]; poly[1,4-cyclohexylenebis(oxyethylene)sebacate-co-

3,3'-(1,4-phenylene)bisacrylate (80:20)]; or poly[1,4-cyclohexylenebis(oxyethylene)terephthalate-co-1-methyl-1-cyclohexene-4,5-dicarboxylateco-5-(N-potassio-p-tolylsulfonamidosulfonyl)-1,3benzenedicarboxylate (10:70:20)].